PB87-152336

Ammonia Emission Factors for the NAPAP (National Acid Precipitation Assessment Program) Emission Inventory

Alliance Technologies Corp., Chapel Hill, NC

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Jan 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB87-152336

EPA/600/7-87/001
January 1987

AMMONIA EMISSION FACTORS FOR THE NAPAP EMISSION INVENTORY

By

David C. Misenheimer
Thomas E. Warn
Sharon Zelmanowitz

ALLIAN[illegible]NOLOGIES CORPORATION
(FORMERLY [illegible]CHNOLOGY DIVISION, INC.)
[illegible]stowne Drive
Chapel Hill, North Carolina 27514

EPA Contract 68-02-3168 (Task 90)

EPA Project Officer: J. David Mobley

Air and Energy Engineering Research Laboratory
Research Triangle Park, North Carolina 27711

This study was conducted in cooperation with the
National Acid Precipitation Assessment Program.

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/7-87/001		PB87 152336/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
Ammonia Emission Factors for the NAPAP Emission Inventory	January 1987
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
D. C. Misenheimer, T. E. Warn, and Sharon Zelmanowitz	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Alliance Technologies Corporation 500 Eastowne Drive Chapel Hill, North Carolina 27514	11. CONTRACT/GRANT NO. 68-02-3168, Task 90
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development **Air and Energy Engineering Research Laboratory** **Research Triangle Park, NC 27711**	Task Final; 1/85 - 12/86 14. SPONSORING AGENCY CODE **EPA/600/13**

15. SUPPLEMENTARY NOTES AEERL project officer is J. David Mobley, Mail Drop 62, 919/541-2612.

16. ABSTRACT The report provides information on certain sources of ammonia emissions to the atmosphere for use in the National Acid Precipitation Assessment Program (NAPAP) emission inventories. Major anthropogenic sources of ammonia emissions to the atmosphere are identified, and emission factors for these sources are presented based on a review of the most recent data available. The emission factors developed are used to estimate nationwide emissions for base year 1980 and are compared to ammonia emission factors used in other emission inventories. Major anthropogenic source categories covered are cropland spreading of livestock wastes, beef cattle feedlots, fertilizer manufacture and use, fuel combustion, ammonia synthesis, petroleum refineries, and coke manufacture. Approximately 840,000 tons of ammonia is estimated to have been emitted in the U.S. in 1980; over 64% of which is estimated to have been from livestock wastes.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Acidification	Pollution Control	13B	07C
Ammonia	Assessments	Stationary Sources	07B	14B
Emission	Wastes	Emission Factors	14G	
Inventories	Livestock	Feedlots	15E	02E
Precipitation (Meteorology)	Fertilizers			02A
	Combustion		04B	21B
Petroleum Refining	Coking		13H	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	**Unclassified**	64
	20. SECURITY CLASS (This page) **Unclassified**	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This report was prepared for the National Acid Precipitation Assessment Program (NAPAP) to provide information on certain sources of ammonia emissions to the atmosphere for use in NAPAP emission inventories. Major anthropogenic sources of ammonia emissions to the atmosphere are identified and emission factors for these sources are presented based on a review of the most recent data available. The emission factors developed are used to estimate nationwide emissions for base year 1980 and are compared to ammonia emission factors used in other emission inventories. Major anthropogenic source categories covered are cropland spreading of livestock wastes, beef cattle feedlots, fertilizer manufacture and use, fuel combustion, ammonia synthesis, petroleum refineries, and coke manufacture. Approximately 8.4×10^5 tons of ammonia are estimated to have been emitted in the U.S. in 1980; over 64 percent of this total is estimated to have been from livestock wastes.

ACKNOWLEDGEMENT

This report was administered by the U.S. Environmental Protection Agency (EPA) with funding from the National Acid Precipitation Assessment Program's (NAPAP) Task Group on Emissions and Controls.

METRIC CONVERSION FACTORS

English Unit	Equivalent Metric Unit
acres	4074 square meters
barrels (bbl)	0.15899 cubic meters
british thermal units/hours (Btu/hr)	0.2931 watts
british thermal units/standard cubic foot (Btu/scf)	37,260 joules/cubic meter
cubic feet (ft^3)	28.316 liters
degrees Farenheit (^oF)	see below*
gallons (gal)	3.785 liters
miles/gallon (mi/gal)	1.6093 kilometers
pounds (lb)	0.45359 kilograms
pounds/barrel (lb/bbl)	2.853 kilograms/cubic meter
pounds/cubic foot (lb/ft^3)	0.01602 kilograms/liter
pounds/gallon (lb/gal)	0.11984 kilograms/liter
pounds/ton (lb/ton)	0.500 kilograms/megagram
square feet (ft^2)	0.0929 square meters
tons	0.90718 megagrams

(*)Temperature in degrees Farenheit (^oF) can be converted to temperature in degrees Celsius (^oC) by the following formula:

$$(^oC) = [(^oF) - 32]/1.8$$

CONTENTS

Page

Abstract..... iii

Acknowledgement..... iv

Metric Conversion Factors..... v

Figures.....viii

Tables.....viii

1. Executive Summary..... 1
2. Introduction..... 9
3. Ammonia Emissions..... 11
   - Introduction..... 11
   - Livestock waste management..... 11
   - Coal combustion..... 11
   - Fuel oil combustion..... 18
   - Natural gas combustion..... 20
   - Mobile sources..... 21
   - Ammonium nitrate manufacture..... 22
   - Anhydrous ammonia fertilization..... 25
   - Petroleum refineries..... 25
   - Ammonia synthesis..... 27
   - Urea manufacture..... 31
   - Coke manufacture..... 32
   - Ammonium phosphate manufacture..... 33
   - Summary..... 34
4. Comparison of NAPAP Ammonia Emission Factors to Factors Developed for Other Inventories..... 35
5. Recommendations..... 39

References..... 46

Appendices

A. Criteria for assessing emission factors..... 48

A-1

LIST OF FIGURES

Number		Page
3-1	Flowsheet for a typical refinery.....	28

LIST OF TABLES

Number		Page
	Metric Conversion Factors.....	iv
1-1	Ammonia Emission Estimates for the 1980 NAPAP Emissions Inventory.....	3
3-1	Ammonia Content in Animal Manures as Percent of Total Nitrogen.....	16
3-2	Ammonia Emissions from Cropland Spreading of Livestock Manure.....	17
3-3	Distribution of Excess Air for Gas Combustion.....	23
3-4	Summary of Ammonia Emission Factors for Mobile Sources.....	24
3-5	Ammonia Emission Factors and Emission Estimates for Ammonium Nitrate Production.....	26
3-6	Summary of Ammonia Emission Factors.....	36
4-1	Comparison of Ammonia Emission Factors.....	40

SECTION 1
EXECUTIVE SUMMARY

The focus of emission inventory activities within the National Acid Precipitation Assessment Program (NAPAP) is to estimate emissions of compounds believed to be involved in the acid deposition process. Ammonia (NH_3) has been identified as a compound that plays a role in atmospheric chemistry relating to acid deposition. This document summarizes the results of a preliminary effort to gather data available for estimating ammonia emissions from significant anthropogenic sources of the compound. The purpose of this effort is to provide the NAPAP Emission Inventory with information for estimating ammonia emissions for base year 1980 and to identify areas where better data are needed.

Because of the limited amounts of data available on ammonia emissions and because of the difficulty in estimating emissions from area sources such as livestock wastes, this document should be considered a first step in developing a complete and accurate ammonia emissions inventory. The reader is cautioned against using the emissions information contained in this document to try to develop an exact assessment of emissions from any particular facility or location. It is possible, in some cases, that orders-of-magnitude differences could exist between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices.

The approach used in developing these emission factors began with a literature search to identify potential emission source categories and to narrow these to major emitters (sources over 100 tons* NH_3/year). Major source categories identified as a result of this effort are listed below:

- Beef cattle feedlots
- Collection of livestock wastes from confined areas and subsequent application to cropland
- Fossil fuel combustion

(*)Readers more familiar with metric units may use the conversion factors near the front of this report to convert to that system.

- Fertilizer manufacture
- Application of anhydrous ammonia to cropland
- Petroleum refineries
- Ammonia synthesis
- Coke manufacture

Potentially significant source categories not included in this document and not currently included in NAPAP's natural sources program are wastewater treatment, range and wild animal excrement, cigarette smoking, forest fires and human breath and perspiration. Further investigation of these sources should be conducted for the NAPAP Emission Inventory for the 1985 base year. Source categories eliminated from the study because of estimated emissions under 100 tons/year or because of a lack of data include cement manufacture, sodium carbonate manufacture, open burning of wood waste, coal refuse piles, and manufacture of a number of synthetic chemicals including fumaric acid, melamine, aniline, and nitroaniline.

After identifying major emission categories, the next step was to determine an appropriate emission factor for each source category. When available, emission factors based on actual emission tests were chosen. Emission factors were evaluated using a methodology analagous to the AP-42 rating system. Factors were rated on a scale of A through E with an A representing data from a large data base covering a good cross section of the industry, and with a high confidence level. Data rated E were developed from a small data base, not necessarily representative of the industry, and with a low confidence level. Ratings of B through D represent data with intermediate confidence levels. Emission factors and associated ratings are listed in Table 1-1.

The emission factors and associated 1980 national emission estimates for each category covered by this report are shown in Table 1-1. The emission estimates presented were calculated by multiplying an assumed level of activity (e.g. production/use rates) for each source category in 1980 by the emission factor for that source category. Activity levels used to estimate nationwide emission in the 1980 NAPAP database were derived from those in the NEDS system.

TABLE 1-1. AMMONIA EMISSION ESTIMATES FOR THE 1980 NAPAP EMISSIONS INVENTORY

Source	Emission factor	Emissions[a] (tons/yr)	Emission factor rating
Livestock Waste Management			
Beef cattle feedlots	13 lbs/animal	150,000	E
Cropland spreading			
beef cattle	1.8 lbs/animal	97,000	E
dairy cows	26 lbs/animal	130,000	E
swine	3.1 lbs/animal	98,000	E
sheep	2.0 lbs/animal	NA	E
laying hens	0.19 lbs/animal	21,000	E
broilers	0.024 lbs/animal	45,000	E
turkeys	0.16 lbs/animal	NA	E
Combustion Sources			
Coal	0.00056 lbs/ton coal[b]	180	E
Fuel oil	0.8 lbs/10^3 gallons fuel[b]	c	E
Natural gas			
utility boilers	3.2 lbs/10^6 ft^3 gas[b]	c	C
industrial boilers	3.2 lbs/10^6 ft^3 gas[b]	c	C
commercial boilers	0.49 lbs/10^6 ft^3 gas[b]	c	C
Mobile sources			
leaded gasoline	0.42 lbs/10^3 gallons fuel[b]	d	D
unleaded gasoline	0.63 lbs/10^3 gallons fuel[b]	d	D
diesel	0.95 lbs/10^3 gallons fuel[b]	d	E
Ammonium Nitrate Manufacture			
Neutralizer	* 18 lbs/ton[e]	36,000	D[e]
Solids formation			
evaporation/concentration	* 17 lbs/ton[e,f]	12,000	D[e]
high density prill towers	* 57.2 lbs/ton[f]	130,000	A
low density prill towers	* 0.26 lbs/ton[f]	67	A
granulators	* 50 lbs/ton[e,f]	47,000	D[e]
high density prill coolers	* 0.04 lbs/ton[f]	9	A
low density prill coolers	* 0.30 lbs/ton[f]	NA	A
low density prill dryers	* 1.6 lbs/ton[e,f]	NA	D[e]
granulator coolers	* 1 lb/ton[e,f]	620	D[e]
Anhydrous Ammonia Fertilizer Application	19 lbs/ton fertilizer	50,000	C
Petroleum Refineries			
FCC units	* 54 lbs/10^3 barrels feed[g]	8,400	B
TCC units	* 6 lbs/10^3 barrels feed[g]	87	B
Reciprocating engine compressors	* 0.2 lbs/10^3 ft^3 gas[b]	NA	B
Ammonia Synthesis			
Carbon dioxide regeneration	* 2.0 lbs/ton[f]	1,500	A
Condensate stripping	* 2.2 lbs/ton[f]	1,600	A

(continued)

TABLE 1-1. (continued)

Source	Emission factor	Emissions[a] (tons/yr)	Emission factor rating
Urea Manufacture			
Solution formation/ concentration	* 18.2 lbs/ton[f]	NA	A
Solid formation			
nonfluidized bed prilling			
agricultural grade	* 0.87 lbs/ton[f]	NA	A
fluidized bed prilling			
agricultural grade	* 2.9 lbs/ton[f]	NA	A
feed grade	* 4.1 lbs/ton[f]	NA	A
drum granulation	* 2.2 lbs/ton[f]	NA	A
rotary drum cooler	* 0.0051 lbs/ton[f]	NA	A
Coke Manufacture			
Oven charging	* 0.02 lbs/ton coal charged	480	D
Door leaks	* 0.06 lbs/ton coal charged	710	D
Coke pushing	* 0.1 lbs/ton coal charged	1,400	D
Quenching (contaminated water)	0.28 lbs/ton coal charged	4,700	D
Ammonium Phosphate Manufacture	* 0.14 lbs/ton[f]	770	A
Minor Point Sources	NA	3,800	-
TOTAL		840,000	

[a]Emission estimates are for 1980.

[b]Refers to pounds ammonia emitted per unit of fuel burned.

[c]NEDS activity levels for fossil fuel combustion sources were not applied to the related emission factors in the Emissions Inventory System. Therefore, emission estimates for these sources categories were not included in the 1980 NAPAP Emissions Inventory.

[d]NEDS activity levels for mobile sources were not applied to the related emission factors in the Emissions Inventory System. Therefore, emission estimates for these source categories were not included in the 1980 NAPAP Emission Inventory.

[e]Emission factor is from mid-point of range reported in AP-42. Associated rating is lower than that reported in AP-42 because of the listing of a single factor rather than a range (as in AP-42).

[f]Refers to pounds ammonia emitted per ton of product.

[g]Refers to pounds ammonia emitted per 10^3 barrels of feed to the cracking unit.

* - Emission factor and associated factor rating is from AP-42.

NA - Not available.

Based on the emission factors chosen and the activity levels assumed for each source category, it is estimated that approximately 8.4×10^5 tons of ammonia were emitted in 1980 from the sources listed in Table 1-1. Over 64 percent of the total is estimated to have been emitted from sources in the livestock waste management category. However, for reasons discussed briefly below, the emission factors used for sources in this category were assigned a low confidence rating, and consequently the nationwide emission estimate for sources in this category should be considered highly uncertain.

The two significant sources of ammonia emissions in the livestock waste management category are cropland spreading and beef cattle feedlots. In cropland spreading, livestock wastes are collected from confined areas and applied to agricultural land. Van Dyne, et al compiled information on amounts of manure used in cropland application. Estimates of ammonia volatilization for various waste management practices and for various types of livestock were calculated from data developed by Hoff, et al and Westerman, et al. Ammonia emission factors for cropland spreading were calculated from these data and were multiplied by 1980 animal population levels in the U.S. to obtain a total emissions estimate of 3.9×10^5 tons NH_3 per year. Cropland spreading is an area source, making it difficult to quantify emissions. Several key assumptions were made in deriving the factors, and the accuracy of these assumptions is uncertain. In addition, volatilization rates from this source will vary considerably with weather conditions and waste management practices. Therefore, the emission factors used, and associated emission estimates for cropland spreading should be considered at best to represent a gross estimate of potential emissions from this source.

The other significant source of ammonia in the livestock waste management category is beef cattle feedlots. Feedlots are areas in which beef cattle are confined for fattening prior to marketing. Because of the large quantity of manure produced in a feedlot, periodic removal is necessary to prevent unacceptable accumulations. Waste management practices other than field spreading include storage in windrows, lagooning, incineration, liming, or pitting. Losses of ammonia from feedlots were reported by Peters, et al, and Hutchinson, et al, from two separate studies. The emission factors reported

in these two studies varied by over three orders of magnitude. Using the average of the two studies, estimated emissions of 1.5×10^5 tons per year were calculated. For reasons similar to those for cropland spreading, the uncertainty of this estimate is substantial and it should also be considered only a gross estimate.

AP-42 emission factors were used to characterize emissions from fertilizer manufacture, ammonia synthesis, petroleum refineries, and coke manufacture. Fertilizers that emit ammonia during the manufacturing process include ammonium nitrate, urea, anhydrous ammonia, and ammonium phosphate. Anhydrous ammonia manufacture is covered under the ammonia synthesis category. Ammonium nitrate is the largest of the fertilizer manufacturing sources, emitting an average of 27 percent of the total from sources listed in Table 1-1. AP-42 emission factors for several sources within the ammonium nitrate fertilizer category vary over several orders of magnitude depending upon whether a plant uses an excess of ammonia or an excess of nitric acid in the process. For the purposes of this study and lacking specific information on the number of plants using excess ammonia, the mid-point of the reported emission factor range was used to estimate nationwide emissions from each of these sources. In the cases where a midpoint emission factor was assumed rather than the range reported in AP-42, the confidence rating for the factor was lowered (below that had been assigned in AP-42) to reflect this assumption. Sources within the ammonium nitrate fertilizer category for which a single emission factor (rather than a range) was reported in AP-42, were given high emission factor confidence ratings as assigned in AP-42.

Emissions from petroleum refineries are primarily from catalytic cracking operations. Sources in the manufacture of coke include oven charging, door leaks, coke pushing, and quenching. Emission factors for both of these source categories were given ratings as assigned in AP-42; a high level of confidence for petroleum refining emission factors and a low level of confidence for coke manufacting factors.

Other sources for which ammonia emission factors were developed include land application of anhydrous ammonia fertilizer and combustion of fuels such as coal, fuel oil, natural gas, and gasoline. Emission factors for these

sources were rated at intermediate to low confidence levels because they were based on small amounts of data as well as data of questionable origin. For example, several emission factors for fuel combustion were found to originate from estimates reported three decades ago that lack a published basis; despite this deficiency, these estimates have been repeated in numerous subsequent reports.

There are several reasons for the deficiencies encountered in the ammonia database. One reason is the lack of a standardized test method for ammonia. Several methods of sampling and analysis were identified in the gathering of data contained in this document. However, none of these have been endorsed by EPA as a standard for ammonia and there appears to be no consensus on which of these methods are the most reliable. Another reason for data deficiencies is the fact that several of the major sources are area sources which are particularly difficult to characterize. Also, no federal mandate exists for the gathering of ammonia emissions data as there is for criteria pollutants and other hazardous compounds. And finally, much of the data that currently exist were gathered during research projects under conditions which are not representative of those found in actual working environments.

Conclusions and recommendations resulting from this effort are:

- The largest anthropogenic source categories of ammonia are:
  - Livestock waste management (64%)
  - Fertilizer production (27%)
- Source test data gathered by reliable test methods for likely operating conditions are needed to better characterize ammonia emissions from the source categories listed below:
  - Livestock waste management
  - Ammonium nitrate manufacture
  - Fertilizer application
  - Fossil fuel combustion
  - Coke manufacture

- The following source categories should be investigated for possible inclusion in the NAPAP Emission Inventory for the 1985 base year:

  - Wastewater treatment
  - Range and wild animal excrement
  - Cigarette smoking
  - Forest fires
  - Human breath and perspiration
  - Natural sources

SECTION 2
INTRODUCTION

The National Acid Precipitation Assessment Program (NAPAP) was established by Congress in 1980 to coordinate and expand research on problems posed by acid deposition in and around the United States. The program is managed through the Interagency Task Force on Acid Precipitation which coordinates eight task groups having specific technical responsibilities. The Task Group on Emissions and Controls is charged with development of comprehensive and accurate inventories of emissions from sources thought to be important in acid deposition processes. One of the compounds identified for inventorying is ammonia.

This document summarizes the results of data gathering activities for ammonia emissions information relating to anthropogenic sources in support of the NAPAP Emission Inventory for base year 1980. Because of the limited amounts of data available on ammonia emissions and because of the difficulty in estimating emissions from area sources such as livestock wastes, this document should be considered a first step in developing a complete and accurate ammonia emissions inventory. The reader is cautioned against using the emissions information contained in this document to attempt to develop an exact assessment of emissions from any particular facility or location. It is possible, in some cases, that orders-of-magnitude differences could result between actual and calculated emissions, depending on differences in source configurations, control equipment, and operating practices.

The approach used in developing these emission factors began with a literature search to identify potential anthropogenic emission source categories and to narrow these to major emitters (source categories over 100 tons NH_3/year). For the purposes of this study, an anthropogenic source of ammonia is considered to be one where ammonia emissions are caused by deliberate and willful activity by man. Sources that are naturally occurring, or that are the result of passive, rather than active, involvement by man are considered to be natural sources. Under these definitions, sources such as chemical manufacturing, fuel combustion, livestock waste management, and fertilizer application are anthropogenic sources while sources such as human

breath and perspiration, and range and wild animal excrement are natural sources. Not all sources are easily categorized under these definitions however, and subjective judgement was used in determining whether certain sources are anthropogenic or natural. For example, although forest fires could be considered to be both a natural and an anthropogenic source of ammonia emissions, in this study it is considered to be a natural source.

The next step in this effort was to determine an appropriate emission factor for each major source category. When available, emission factors based on actual emission tests performed by a sound methodology and accompanied by adequate background data were used. Emission factors were evaluated on a scale of A through E, as in AP-42, with an A representing data from a large data base covering a good cross section of the industry, and with a high confidence level. Data rated E were developed from a small data base, not necessarily representative of the industry, and with a low confidence level. Ratings of B through D represent data with intermediate confidence levels. Criteria used in determining emission factor ratings are discussed in more detail in Appendix A.

After identifying the best emission factors for each source, these factors were multiplied by the corresponding source activity rates for base year 1980 to determine the relative importance of each source.

SECTION 3
AMMONIA EMISSIONS

INTRODUCTION

Atmospheric ammonia is emitted in appreciable quantities by both natural and anthropogenic sources. In this section, emission factors and total annual ammonia emission estimates are developed for major anthropogenic sources including fossil fuel combustion, domestic animal waste management, manufacture and application of fertilizers, ammonia synthesis, and coke manufacture. Emission factors are evaluated on a scale of A through E, with an A representing the more reliable emission factor and a rating of E, the lesser. A discussion of the criteria used to evaluate the emission factors is located in Appendix A.

Anthropogenic sources of ammonia emissions not included in this report due to low emissions estimates (below 100 tons NH_3/year) or lack of data include cement manufacture, sodium carbonate manufacture, open burning of wood waste, coal refuse piles, and manufacture of several synthetic materials such as fumaric acid, melamine, an-line and nitroaniline.

LIVESTOCK WASTE MANAGEMENT

Excrement from livestock and poultry is a major source of ammonia emissions. Livestock wastes contain inorganic nitrogen which is readily released through several mechanisms including ammonia volatilization, nitrification, denitrification, leaching and runoff. Ammonia volatilization contributes significantly to the total loss of nitrogen from livestock wastes.

The two major sources of ammonia emissions in the livestock waste management category are beef cattle feedlots and cropland spreading. Beef cattle feedlots are areas in which beef cattle are confined for fattening prior to marketing. In cropland spreading, livestock and poultry wastes are

collected from confined areas and applied to agricultural land. These source categories are discussed in more detail below.

Beef Cattle Feedlots

Production of beef cattle can be divided into four stages: calf production, backgrounding, finish feeding, and slaughtering. During calf production, the calves are raised in pastures with other cows to weaning weights of about 400 pounds. Backgrounding consists of developing the calves from weaning to weights of 550 to 700 pounds. This usually is achieved by grazing them in pastures or keeping them in feedlots where they are fed harvested roughage and grain. Development from newborn calf to adult beef animal ready for finish feeding requires about 20 months. The finish feeding, or fattening process, typically lasts four or five months, during which time the cattle are confined in a feedlot and fed a high energy ration of feed grains until they reach slaughter weight of about 1,100 pounds.[2]

Wastes excreted by cattle grazing in pastures or range areas are dispersed, allowing the soil to assimilate the excrement. However, manure produced in feedlot situations must be removed and processed because of space restrictions. Animal manure contains complex carbohydrates, proteins, and fats, which are metabolized into simpler compounds by microorganisms. In the presence of oxygen, the end products of metabolism are heat, CO_2, and H_2O. This process, called aerobic metabolism, is dependent upon temperature, oxygen, and moisture. In the absence of oxygen, however, anaerobic metabolism occurs with ammonia as an end product.[2]

Ammonia is the predominant gaseous pollutant emitted from feedlots. Ammonia is a result of anaerobic decomposition of feedlot surfaces as well as volatilization from urine. Ammonia emissions are generally increased when conditions favor anaerobic decay. Although 25 to 40 percent moisture levels

are necessary on feedlot surfaces for aerobic decomposition (which is odorless), too much rain or watering, resulting in puddling and wet spots, can trigger increased ammonia production. Ammonia formation may also occur when anaerobic conditions exist in manure stockpiles and runoff holding ponds. In general, higher ammonia emissions are associated with higher temperature and humidity, overly wet conditions, and feedlot disturbances such as mounding or manure removal.[3]

Ammonia control is best effected by housekeeping measures that enhance aerobic rather than anaerobic decomposition of the cattle wastes. For example, aside from reducing dust emissions, sprinkling provides moisture for aerobic biodegradation of the manure. Good drainage must be provided, however, and overwatering must be avoided. Deep accumulations of manure of slurry consistency can optimize anaerobic conditions. Hence, feedlot surfaces should be periodically scraped to remove such accumulations. Scraping should be done carefully, so that only the surface layer is disturbed. Manure stockpiles should not be allowed to get too large, too wet, or encrusted, and they should be disposed of within four or five days. If the stockpiles are composted, the manure should be piled in long narrow windrows to allow access for turning the piles to promote aerobic conditions and to enable rapid control of spontaneous combustion fires. Anaerobic conditions can be reduced in runoff holding ponds by removing solids from the runoff, by adding more water to the ponds to dilute the nutrient content, and by aeration of the surface. Runoff water also may be treated chemically to suppress the release of malodorous gases.[3]

In a study of ammonia emissions from beef cattle feedlots,[2] 56 data points for untreated pens under varying temperature and humidity conditions were given. During sampling, a sampling box was placed on the feedlot surface. The box covered a square area of 0.37 m^2 with a plywood deck 0.3 m from the bottom. Air was pulled from beneath the deck through an absorption tube containing 10 ml of dilute sulfuric acid. The ammonia concentration of the absorbing acid solution was measured by nesslerization. The 56 data points ranged from 0.27×10^{-6} lbs/ft^2-hr to 10.4×10^{-6} lbs/ft^2-hr, with a mean of 2.97×10^{-6} lbs/ft^2-hr.

Another study of emissions was conducted at a cattle feedlot in northeastern Colorado.[4] Ammonia emissions were collected for periods of 1 to 3 hours at eight different heights above the feedlot surface by drawing air through bubblers containing dilute sulfuric acid. The collection efficiency of the bubblers was determined to be greater than 99 percent. The bubbler solutions were analyzed for ammonia by the indophenol method[5] and by GC analysis of a pentafluorobenzamide derivative of ammonia. Daily samples ranged from 15.9×10^{-6} lbs/ft^2-hr to 58.9×10^{-6} lbs/ft^2-hr, with a mean value of 34.8×10^{-6} lbs/ft^2-hr.

A representative feedlot was chosen as one that feeds and markets 14,800 head each year with a capacity of 8,000 head at any one time on a square area of 27.5 acres.[2] The average of the emission factors above was applied to the representative feedlot to obtain an emission factor of 13 lbs NH_3 per year per head of cattle marketed. This factor should be considered at best to be a crude estimate of potential emissions from feedlots where little or no special housekeeping measures are employed to control the release of gases. A rating of E (see Appendix A) is assigned to this factor because of the uncertainty of its representativeness. Multiplying the emission rate by the total number of feedlot cattle reported in the 1980 National Emissions Data System (NEDS) database[6] (2.3×10^7 cattle) results in an estimate of 150,000 tons of ammonia from beef cattle feedlots.

Ammonia from Cropland Spreading

The other major source of ammonia emissions in the livestock waste management category is the spreading of livestock and poultry manure on cropland. Several factors affect the amount of ammonia volatilized from cropland-spread manure including soil type, manure characteristics, atmospheric conditions and manure application method.

High soil and manure pH values lead to large ammonia volatilization losses, because as pH increases, the equilibrium reaction between NH_3 (ammonia gas) and NH_4^+ (ammonium ion) is driven toward greater NH_3 production. Peters and Reddell[7] found greater ammonia losses from beef manure applied to limed soil columns compared with beef manure applied to unlimed soil columns.

Soil texture and cation exchange capacity affect ammonia volatilization losses. Crane, et al[8] reported that volatilization of ammonia is less from soils with a high cation exchange capacity. Apparently, this is due to an increase in the soil's capacity to adsorb and retain ammonium ions as cation exchange capacity increases.

Soil moisture has an effect on volatilization of ammonia from soil/manure systems, particularly when manure is injected rather than surface-applied. A dry soil tends to discourage ammonia losses to a greater extent than does a wet soil. Temperature and wind velocity increases tend to increase ammonia volatilization potential. Steenhuis, et al[9] measured greater volatilization losses from dairy manure exposed to higher temperatures and wind speeds.

Ammonia emission factors for land-spreading of livestock and poultry manure were estimated based on manure production and characterization data. Data characterizing chemical properties of various manures were compiled by Westerman, et al.[10] Included in these data are the ammonia contents of manures as a percentage of total nitrogen as presented in Table 3-1. The percentages of total nitrogen as ammonia for manure that has been scraped, slurried, and held in lagoons were averaged to obtain estimated percentages over the various waste management systems.[10] In order to define an average ammonia content over various livestock groups, a weighted average was calculated based on the relative proportions of nitrogen produced in dairy cows, beef cattle, swine, and poultry manure as presented in Table 3-2. Thus, averaged over animal groups and waste management schemes, approximately 50 percent of the total nitrogen in manure is in ammoniacal form.

To estimate ammonia emissions, volatilization losses were quantified. The percent ammonia volatilized relies heavily on manure application method. Westerman, et al[10] reviewed the literature on ammonia loss from surface-applied manure and estimated an 80 percent loss of ammonia applied as solid manure and a 60 percent loss of ammonia applied as liquid manure, 7 days after spreading. Assuming equal amounts of solid and liquid manure are surface-applied and in view of the fact that most ammonia loss occurs within a few days after application, the average ammonia loss is estimated to be 70 percent when surface-applied. For ammonia loss from injected manure, a 25 percent loss reported by Hoff, et al[11] was used. Assuming that 25 percent

TABLE 3-1. AMMONIA CONTENT IN ANIMAL MANURES AS PERCENT OF TOTAL NITROGEN[10]

Manure type	Dairy cows	Beef cattle	Swine	Poultry
Fresh	3	32	52	33
Scraped	24	5	28	58
Slurry	39	38	64	75
Lagoon	67	71	81	86
Average*	43	38	58	73

*Percentages were averaged for manure that was scraped, slurried, and held in lagoons.

TABLE 3-2. AMMONIA EMISSIONS FROM CROPLAND SPREADING OF LIVESTOCK MANURE

Animal	Manure production[a] (10^3 tons/yr)		Manure for spreading[a] (10^3 tons/yr)		Emission factors[b] (lbs NH_3/animal-yr)	Animal population (1980)[c]	Emissions (tons/yr)
	Manure	N	Manure	N			
Cattle	62,485	1,666	17,897	304	1.8	1.08×10^8	97,000
Dairy cows	25,210	814	20,358	498	26	9.98×10^6	130,000
Swine	13,360	1,086	5,538	284	3.1	6.30×10^7	98,000
Sheep	3,796	147	1,700	48	2.0	NA	NA
Laying hens	3,374	158	3,259	92	0.19	2.23×10^8	21,000
Broilers	2,086	136	2,434	122	0.024	3.73×10^9	45,000
Turkeys	1,251	76	983	36	0.16	NA	NA
TOTAL	111,562	4,083	52,169	1,384			390,000

[a]Reference 12.

[b]Calculated by multiplying nitrogen available for spreading by 50 percent (percent of total nitrogen as ammonia) and by 59 percent (percent of ammonia in manure that volatilizes) and dividing by animal populations for 1974 (Reference 12).

[c]Reference 6.

NA - Not available.

of manure spread is injected and 75 percent is surface-applied, a weighted average over application methods results in an overall ammonia loss of 59 percent of applied ammoniacal nitrogen.

Multiplying the amounts of nitrogen available for land spreading for the various livestock categories in 1974 (Table 3-2) by the factors calculated above (50 percent of total nitrogen as ammonia and 59 percent loss by volatilization of ammonia spread) and dividing by animal population levels for 1974,[13] emission factors were calculated as presented in Table 3-2. These factors were multiplied by animal population data for 1980[6] to calculate total emissions for the animal groups. This data is also listed in Table 3-2. Total emissions from cropland spreading of livestock waste are estimated at 390,000 tons ammonia for 1980.

COAL COMBUSTION

General[14]

Coal types are broadly classified as anthracite, bituminous, subbituminous, or lignite. Further classification is made based on heating values and amounts of fixed carbon, volatile matter, ash, sulfur, and moisture. Pulverized coal and cyclone furnaces are used primarily in utility and large industrial boilers and stokers are used extensively in small to medium industrial boilers. Ammonia emissions may vary with fuel type and firing mechanism. However, data available do not support a distinction on this basis.

Emission Control Techniques[14]

Scrubbers, electrostatic precipitators (ESP), cyclones, and baghouses are used frequently as flue gas control techniques. However, they are designed primarily to control particulate matter from flue gas streams and have little

effect on the reduction of ammonia. In fact, ammonia emissions may increase in ESP's where ammonia is added as a conditioning agent to improve fly ash precipitation.

Gaseous sulfur compounds typically are removed from flue gas streams by flue gas desulfurization (FGD) systems. FGD systems would be expected to remove ammonia from the gas stream along with sulfur compounds.

Emissions

Historically, relatively large ammonia emission factors have been reported for coal combustion. A 1945 report[15] presented an emission factor of 2.6 lbs NH_3/ton coal burned. A 1956 study[16] of air pollution reported ammonia emissions at 2 lbs NH_3/ton coal from the public consumption of coal, although no information was presented on the origin of the factor. This factor has been used in numerous subsequent reports[17-22] despite the lack of a published basis for its validity. In 1976, emissions were measured at a level of about 1 lb NH_3/ton coal for a 200,000 Btu/hr laboratory boiler fired with bituminous coal.[23] However, this factor is based on only one sample and is therefore also uncertain.

Results published in 1985 for a coal-fired power plant in Portage, Wisconsin are orders of magnitude lower than the above emission rate estimates. Ammonia emissions from the power plant were measured over a 6-month period in 1980.[24] The plant operates two 527-MW pulverized-coal furnaces that utilize electrostatic precipitators to control particulate emissions. Unit I, which came on line in the early 1970s, has a 107 meter stack and was burning a western bituminous coal. Ammonium carbonate was added to Unit I to improve particulate collection efficiency in the ESP. Unit II, which came on line in the mid-1970s, has a 198 meter stack and was burning another bituminous coal. During the sampling period, the combustion units were operating near full capacity, consuming about 2×10^5 kg dry coal/hr. Six samples were collected per combustion unit over the sampling period. Samples were collected with a 1.5 meter heatable glass probe in conjunction with a cyclone, a filter holder in a heatable box, four impingers in series in an ice bath, and a meter case, consisting of manometer, pumps, and dry gas meter bracketed by thermometers.

Ammonia was captured in the first two impingers which were each filled with 100 ml of 0.5 M H_2SO_4 and was determined potentiometrically by standard addition with an Orion Model 95-10 NH_3 gas electrode and an Orion 801 meter.

Emissions from Unit I averaged 4.7 kg NH_3/hr for the sampling period while emissions from Unit II averaged only 0.056 kg NH_3/hr. The larger emissions from Unit I presumably resulted from the addition of ammonium carbonate. The ammonium carbonate addition in Unit I is not representative of current operating practices used in pulverized-coal combustion, and therefore the emission factor for Unit I is not used in this study.

The emission factor for Unit II calculated from the operating capacity above is 0.00056 lbs NH_3/ton coal combusted. This emission factor was used for ammonia emissions from coal combustion in the NAPAP inventory. However, emissions tests for other combustion units burning a variety of coals are needed to better characterize emissions from the source category. Because of the limited representativeness of the emission factor, a rating of E was assigned (see Appendix A).

The activity level reported for coal combustion in the 1980 NEDS database[6] is 6.32×10^8 tons coal combusted. Based on the emission factor for Unit II above, 180 tons of ammonia were emitted as a result of coal combustion in 1980.

FUEL OIL COMBUSTION

Ammonia emissions from fuel oil combustion have been reported based on two broadly classified types of fuel oils, distillate and residual. The primary use of distillate oils (fuel oil grade Nos. 1 and 2) is in domestic and small commercial appliances in which simple fuel burning is required. Distillates are more volatile and less viscous than residual oils, having negligible ash and nitrogen contents. Residual oils (grade Nos. 4, 5 and 6) are used mainly in utility, industrial, and large commercial applications with sophisticated combustion equipment. Residual oils must be heated to facilitate handling and proper atomization. Because residual oils are produced from the residue left

after lighter fractions (gasoline, kerosene, and distillate oils) have been removed from the crude oil, they contain significant quantities of ash, nitrogen, and sulfur.[25]

Ammonia emissions from fuel oil combustion were estimated over three decades ago to range from 0.06 to 8 lbs/1000 gallons of fuel oil burned.[26,16] A more recent study (1976) of a 200,000 Btu/hr laboratory combustion unit that was operated at 2 percent excess air and fueled with No. 6 residual oil resulted in emissions of 2.54 ppm NH_3 and 20 ppm NH_3 for the two samples taken.[27] Emission factors of 0.19 lbs NH_3/1000 gallons oil burned and 1.5 lbs NH_3/1000 gallons oil burned (average of about 0.8 lbs/1000 gallons) were calculated based on fuel feed and flue gas rates. The validity of this emission factor is questionable since it is based on only two data points. Further testing is needed to accurately quantify emissions from distillate and residual oil combustion.

NEDS activity levels for the fuel oil combustion source category were not applied to the emission factors in the Emissions Inventory System (EIS). Therefore, emission estimates for this source category were not included in the 1980 NAPAP emissions inventory.

NATURAL GAS COMBUSTION

Natural gas is used throughout the U.S. for power generation, industrial process steam and heat production, and domestic and commercial space heating. The primary component of natural gas is methane, although varying amounts of ethane and smaller amounts of nitrogen, helium, and carbon dioxide are also present. The average gross heating value of natural gas usually varies from 1000 to 1100 BTU/scf. Because natural gas in its original state is a gaseous, homogeneous substance, its combustion is simple and can be controlled precisely. Common excess air rates range from 10 to 15 percent, but some large units operate at lower excess air rates to increase efficiency and reduce nitrogen oxide (NO_x) emissions.[28]

Ammonia emission rates were estimated in several studies from two to three decades ago to range from 0.3 to 20 lbs $NH_3/10^6$ ft^3 gas burned.[26,29,30] Information on the basis of these emission factors was not available. A study

published in 1976 on a 200,000 Btu/hr laboratory gas combustor reported emission factors of 3.25, 1.35, and 0.22 kg $NH_3/10^9$ Btu at excess oxygen levels of 2, 4, and 6 percent, respectively.[31] Based on an average heating value of 1000 Btu/scf, these factors are equal to 7.2, 3.0, and 0.49 $lbs/10^9$ ft^3. These factors are averages of 17 tests, 23 tests, and 15 tests, respectively.

Cass, et al,[10] recommended distributions of excess oxygen conditions among natural gas combustion sources as presented in Table 3-3. Emission factors for each combustion source listed in Table 3-3 were calculated by applying the excess oxygen distributions to the above emission factors.

NEDS activity levels for the natural gas combustion source category were not applied to the emission factors in the EIS. Therefore, emission estimates for this source category were not included in the 1980 NAPAP emissions inventory.

MOBILE SOURCES

Mobile sources of ammonia emissions are represented by the diverse population of motor vehicles powered by fossil fuel combustion. These mobile sources utilize a wide variety of internal combustion engines which vary in their size, operational parameters (e.g., fuel type, engine temperature, RPMs), efficiency, engine age, emission control equipment, and frequency of use. This variability complicates the calculation of ammonia emission factors for mobile sources.

The results of several studies that were conducted to determine the concentration of ammonia present in automotive exhaust are presented in Table 3-4. By averaging the appropriate emission factors, ammonia emission factors of 0.42 lbs NH_3/gallon, 0.63 lbs NH_3/gallon, and 0.95 lbs NH_3/gallon were developed for leaded gasoline, unleaded gasoline and diesel fuel, respectively. It should be noted however, that these emission factors were derived from a limited amount of experimental data.

NEDS activity levels for the mobile source category were not applied to the emission factors in the EIS. Therefore, emission estimates for this source category were not included in the 1980 NAPAP emissions inventory.

TABLE 3-3. DISTRIBUTION OF EXCESS AIR FOR GAS COMBUSTION

Source	Percent of Sources			
Category	2% Excess Air[a]	4% Excess Air[b]	6% Excess Air[c]	Emission Factor
Utility boilers	33	22	45	3.2 lbs/10^9 ft^3
Industrial boilers	35	15	50	3.2 lbs/10^9 ft^3
Commercial boilers	0	0	100	0.49 lbs/10^9 ft^3
Space heaters	0	0	100	0.49 lbs/10^9 ft^3
Refinery process heaters	19	33	48	2.6 lbs/10^9 ft^3

[a]Corresponds to ammonia emission factor of 7.2 lbs/10^9 ft^3.

[b]Corresponds to ammonia emission factor of 3.0 lbs/10^9 ft^3.

[c]Corresponds to ammonia emission factor of 0.49 lbs/10^9 ft^3.

TABLE 3-4. SUMMARY OF AMMONIA EMISSION FACTORS FOR MOBILE SOURCES

Reference	Description	NH_3 Concentration	Emission Factor[a] (lb. NH_3/1000 gal. fuel)
Henein (1975)[32]	used vehicle, catalytic converter, unleaded gasoline	10 ppm[b]	0.56
	used vehicle, without catalytic converter, unleaded gasoline	21 ppm	1.16
	Puegeot 504 D Car; #2 Diesel Fuel	11 ppm	0.95
Gentel (1973)[33]	1972 Pontiac 400 CID V-8, without catalytic converter, unleaded gasoline	12 ppm	0.67
	1972 Pontiac 4 CID V-8, catalytic converter, unleaded gasoline	10 ppm	0.56
	1972 Pontiac 4 CID V-8, leaded gasoline	13 ppm	0.71
Harkins and Nicksic (1967)[34]	1956 Oldsmobile V-8 engine, leaded gasoline	2 ppm	0.12
Cadle and Mulawa (1980)[35]	unleaded gasoline engine, catalytic converters	4.9 mg/mile	0.18[c]

[a]Assuming air-to-gasoline ratio of 15 by weight and a gasoline density of 6.19 lbs/gallon, or an air-to-diesel ratio of 22 by weight and a diesel fuel density of 7.05 lbs/gallon.

[b]Average of reported values.

[c]Calculated assuming 16.9 miles/gallon (EEA, 1984).[36] Additionally, 4.9 mg/mile was the reported average for this study.

AMMONIUM NITRATE MANUFACTURE

Ammonium nitrate is produced by mixing nitric acid and ammonia in a reactor or neutralizer. Either ammonia or nitric acid are emitted from the neutralizer, depending upon which reactant is added in excess to the process. Most plants today operate the neutralizer with excess ammonia. An 83 percent aqueous ammonium nitrate solution is produced in the neutralizer and may be sold for use as a fertilizer or further concentrated for use in solid ammonium nitrate formation. Solid ammonium nitrate may be produced by prilling, graining, granulation, or crystallization. The following steps are involved in solids production: evaporation/concentration, solidification, particle characterization, and finishing.[37]

Ammonia emission factors for ammonium nitrate manufacture are from AP-42 and are listed in Table 3-5. Emissions vary depending upon specific plant operating characteristics such as the use of excess ammonia or acid in the neutralizer. For the neutralizer, evaporator concentrator, granulators, low density prill dryers, and granulator coolers, emission factor ranges were reported in AP-42. For these sources, a mid-point was used to calculate emissions in the NAPAP database as shown in Table 3-5. These emission factors were assigned a D rating (see Appendix A) because of the limited data available to support a single factor. All other factors were assigned an A rating as was assigned in AP-42.

Emission estimates for ammonia from ammonium nitrate manufacture are based on activity rates from the 1980 NEDS database.[6] Emission estimates are presented in Table 3-5 and total 225,000 tons ammonia for base year 1980.

ANHYDROUS AMMONIA FERTILIZATION

Underground injection of anhydrous ammonia fertilizer has been identified as a source of ammonia emissions from agricultural land. In a test conducted on 64.8 acres of land, anhydrous ammonia was injected into the ground by means of an injection bar, pulled by a tractor, with six tool shanks positioned at intervals of 40 inches along the bar. Attached to each shank was a delta-wing foot which lifted the soil and allowed ammonia to be injected horizontally

TABLE 3-5. AMMONIA EMISSION FACTORS AND EMISSION ESTIMATES FOR AMMONIUM NITRATE PRODUCTION

Source	Emission factors[a] (lbs NH_3/ton product)	Activity rate[b] (tons/yr)	Emissions (tons/yr)
Neutralizer			
granulator	18[c]	1.0×10^6	9,100
high density prilling	18[c]	2.3×10^6	20,000
low density prilling	18[c]	7.6×10^5	6,800
Solids formation			
evaporation/concentration			
high density	17[c]	1.2×10^6	10,000
low density	17[c]	2.2×10^5	1,900
high density prill towers	57.2	4.5×10^6	130,000
low density prill towers	0.26	5.2×10^5	67
granulators	50[c]	1.9×10^6	47,000
high density prill coolers	0.04	4.4×10^5	9
low density prill coolers	0.30	NA	NA
low density prill dryers	1.6[c]	NA	NA
granulator coolers	1[c]	1.2×10^6	622
TOTAL			225,000

[a]From AP-42 (Reference 37).

[b]From 1980 NEDS database (Reference 6).

[c]Emission factor is from mid-point of range reported in AP-42.

under it. The injection tube split off into two branches at each delta-wing which resulted in a total of 12 injectors with a spacing of 20 inches between each injector.[38]

Ammonia was injected at a rate of 583 pounds nitrogen per acre at an average injection depth of 4.9 inches. Ammonia emissions were measured in air samples collected in acidified traps. Sampling data resulted in an average emission rate of 5.43 pounds nitrogen per acre with a maximum error of no more than 20 percent. This is a loss of approximately 19 pounds of ammonia per ton of ammonia applied. This level of emissions may be higher than normal due to the fact that the soil that was tested was heavy clay, with a pH of 8.2, low in organic matter, and very moist at the time of injection so that the disturbed soil did not fall back readily to cover the opening made by the injector. This emission factor was assigned a C rating. Ammonia emissions from this source are estimated at a level of 50,000 tons based on the 1980 NEDS activity rate of 5.3×10^6 tons fertilizer.[6]

PETROLEUM REFINERIES

Ammonia emissions were reported for several sources in petroleum refinery processes in a 1958 study conducted by the County of Los Angeles.[39] Sources emitting ammonia include catalyst regeneration in fluid and moving bed catalytic cracking units, and reciprocating engine compressors used in high pressure operations such as hydrodesulfurization, isomerization, reforming, and hydrocracking. Ammonia is emitted in flue gas from catalyst regeneration and as a combustion product in the exhaust gas of compressor engines.

The petroleum refining industry employs a wide variety of processes. A refinery's processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The example refinery flow scheme presented in Figure 3-1 shows the general processing arrangement used by refineries in the United States for major refinery processes. The arrangement of these processes varies among refineries and few, if any, employ all of these processes.[40]

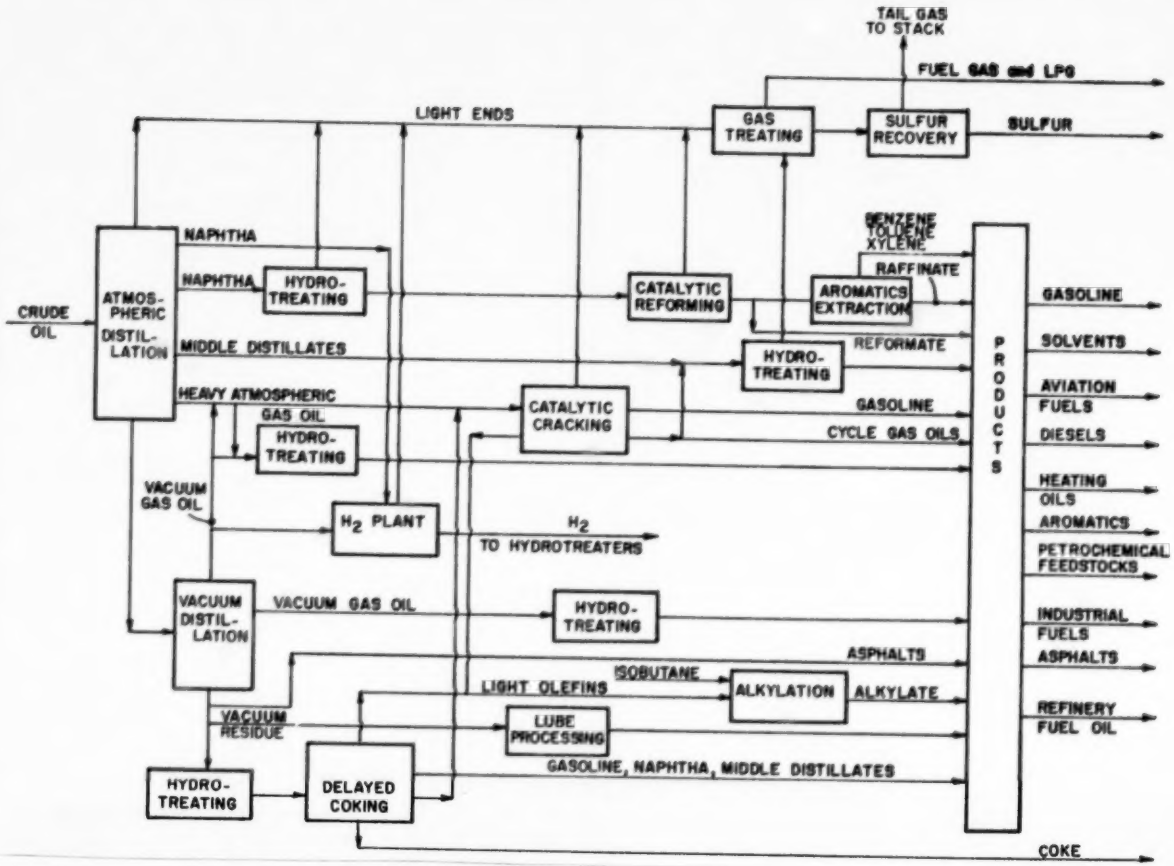

Figure 3-1. Flowsheet for a typical refinery.[40]

Ammonia from Catalyst Regeneration

One of the most important processes used in petroleum refineries is catalytic cracking. In the presence of catalysts, pressure, and heat, heavy oils are cracked into lighter hydrocarbons during catalytic cracking to produce gasoline and distillate blending components. This is accomplished by use of either fluid catalytic cracking units or moving-bed catalytic cracking units.[40]

In the fluid catalytic cracking (FCC) unit, hot catalyst particles and preheated fresh oil feed are introduced into the bottom of a vertical transfer column where the feed is vaporized. As the catalyst and oil mix and flow upwards into the reactor, the cracking reactions occur. In the reactor, the hydrocarbon vapors are separated from the catalyst particles by cyclones. The spent catalyst falls to the bottom of the reactor and is steam stripped as it exits the reactor bottom to remove adsorbed hydrocarbons. The catalyst then is combusted in the regeneration step to remove coke deposited as a result of the cracking reactions.

Moving bed catalytic cracking (known as Thermofor catalytic cracking or TCC) employs catalyst beads that flow by gravity into the top of the reactor and contact a mixed-phase hydrocarbon feed. Cracking reactions take place as the catalyst and hydrocarbons move concurrently downward through the reactor to a zone where the catalyst is separated from the vapors. The gaseous reaction products flow out of the reactor to the fractionation section of the unit. The catalyst is steam stripped to remove any adsorbed hydrocarbons. It then falls into the regenerator where coke is burned from the catalyst. The regenerated catalyst is separated from the flue gases and recycled to be mixed with fresh hydrocarbon feed.

Flue gas from catalyst regeneration FCC and TCC units is a source of ammonia emissions as well as emissions of hydrocarbons, oxides of sulfur, aldehydes, oxides of nitrogen, cyanides, carbon monoxide, and particulates. Gaseous emissions from the FCC unit can be controlled by wasteheat boilers. TCC catalyst regeneration produces smaller quantities of emissions than the FCC unit. Pollutants from the TCC unit can be incinerated by passing the flue

gases through a process heater fire-box or smoke plume burner. Uncontrolled emission factors for the FCC and TCC units have been estimated at 54 and 6 pounds ammonia per 10^3 barrels fresh feed, respectively.[40] These emission factors were given a rating of B as assigned in AP-42. Activity rates of 3.1 x 10^8 barrels fresh feed for FCC units and 2.9 x 10^7 barrels fresh feed for TCC units were taken from the 1980 NEDS database[6] and were used to calculate total uncontrolled emissions of 8,500 tons ammonia.

Ammonia from Engine Compressors

Another source of ammonia in petroleum refineries is reciprocating engine compressors. Many older refineries run high pressure compressors with reciprocating and gas turbine engines fired with natural gas. In the past, natural gas was a cheap, abundant source of energy. Examples of refining operations that require high pressure include hydrodesulfurization, isomerization, reforming, and hydrocracking. Compressors powered by reciprocating engines are less reliable and harder to maintain than those powered by steam engines or electric motors. For this reason and because of increasing natural gas costs, very few such units have been installed in the last few years. The major source of ammonia emissions from reciprocating engines is combustion products in the exhaust gas. The emission factor for ammonia from reciprocating engine compressors has been estimated at 0.2 pounds per 10^3 cubic feet of gas burned.[40] Other emissions include carbon monoxide, hydrocarbons, nitrogen oxides, and aldehydes. Operating rate information for compressor engines at petroleum refineries is available in NEDS. However, much of the information is confidential, and therefore a complete listing of reciprocating engine compressor usage data is not available.

AMMONIA SYNTHESIS

Anhydrous ammonia is synthesized by reacting hydrogen with nitrogen at a molar ratio of 3:1, then compressing the gas and cooling it to -27°F (-33°C). In the United States, about 98 percent of synthetic ammonia is produced by catalytic steam reforming of natural gas.[41]

Seven process steps are required to produce synthetic ammonia by the catalytic steam reforming method:

- Natural gas desulfurization
- Primary reforming with steam
- Secondary reforming with air
- Carbon monoxide shift
- Carbon dioxide removal
- Methanation
- Ammonia synthesis

The first, fourth, fifth, and sixth steps are to remove impurities such as sulfur, CO, CO_2, and water from the feedstock, hydrogen, and synthesis gas streams. In the second and third steps, hydrogen is manufactured and nitrogen is introduced into the process. The seventh step produces anhydrous ammonia from synthetic gas. While all ammonia plants use this basic process, details such as pressures, temperatures, and quantities of feedstock vary from plant to plant.[41]

Ammonia emissions occur during regeneration of carbon dioxide scrubbing solution and steam stripping of process condensate. Carbon dioxide is removed from the synthesis gas by scrubbing with monoethanolamine or hot potassium carbonate solution. Regeneration of this CO_2 scrubbing solution with steam produces emissions of ammonia. Cooling the synthesis gas after low temperature shift conversion forms a condensate containing quantities of NH_3, CO_2, methanol, and trace metals. Condensate steam strippers are used to

remove NH_3 and methanol from the water, and steam from this is vented to the atmosphere, emitting NH_3, CO_2, and methanol.[41]

The ammonia emission factors for carbon dioxide regeneration and condensate stripping are 2.0 and 2.2 pounds per ton of product, respectively, as described in AP-42.[50] A rating of A was assigned to the factors in AP-42. Applying these factors to the activity rates in the 1980 NEDS database[6] (1.5×10^6 tons NH_3 and 1.4×10^6 tons NH_3, respectively) results in a total emission estimate of 3,100 tons.

UREA MANUFACTURE

Urea is produced by reacting ammonia and CO_2 to form ammonium carbamate, which is then hydrated to form urea. There are over 15 production methods that can carry out these reactions. While the basics of the processes are the same, variations occur in vessel design, operating conditions, and type and quantity of recycle of unreacted material.

Emissions from urea manufacture consist of ammonia and particles of solid urea. In solution production, ammonia is emitted from the solution concentration step, and in solid production it is emitted from the prilling tower, granulator, and rotary drum cooler.[42]

The emission factor for solution concentration is 18.2 lbs NH_3/ton product. In solids formation, the emission factor for agricultural grade nonfluidized bed prilling is 0.87 lbs NH_3/ton product. Emission factors of 2.9 lbs NH_3/ton product and 4.1 lbs NH_3/ton product were developed for agricultural grade and feed grade fluidized bed prilling, respectively. Emission factors for drum granulation and rotary drum coolers are 2.2 lbs NH_3/ton product and 0.0051 lbs NH_3/ton product. A rating of A was assigned to these emission factors in AP-42. No activity rate was reported for these sources in the 1980 NEDS database, therefore no emissions estimate was calculated.

COKE MANUFACTURE

Coking is the process of destructive distillation or the heating of coal in an atmosphere of low oxygen content. In the primary method of coke manufacture, the byproduct method, bituminous coal is heated in ovens to remove the volatile components. The volatile components are recovered and processed in the byproduct plant to produce ammonia, coke oven gas, tar, phenol, light oil (benzene, toluene, and xylene), and pyridine. The residue that remains in the oven is coke. The byproduct method accounts for more than 98 percent of U.S. coke production.[43]

Narrow rectangular slot-type coking ovens constructed of silica brick are used in the byproduct method. A battery is commonly made up of a series of 40 to 70 of these ovens interspaced with heating flues. A larry car runs along the top of the coke battery, charging the ovens with coal through the ports. After each charging, the ports are sealed, and heat is supplied to the ovens by combustion of gases passing through the flues between the ovens. The fuels used in the combustion process are natural gas, coke oven gas, and blast furnace gas. In the ovens, coke is formed first near the brick walls and then toward the center, where temperatures are 2000°-2100°F. After a period of 16-20 hours, the coking process is complete. Coke is pushed by a ram from the oven into a quenching car. The quenching car of hot coke is moved by rail to the quench tower, where several thousand gallons of water are used to cool the coke. The coke is allowed to dry and is separated into various sizes for future use.[43]

Ammonia emissions originate from the following byproduct coking operations: (1) charging of coal into the incandescent ovens, (2) oven leakage during the coking period, (3) pushing the coke out of the oven, and (4) quenching the hot coke. Of these operations, the quenching step is the major source of NH_3 emissions.[43]

Coke is commonly quenched in this country with water contaminated by plant process waste streams and by prior quenching. The contaminants entrained in the water evaporate or decompose on contact with the hot coke and are discharged to the atmosphere with the water vapor. Thus, emissions from coke quenching depend on the makeup of the water used for quenching.[44]

Emission factors for oven charging, door leaks, coke pushing, and quenching are 0.02 lbs/ton coal charged, 0.06 lbs/ton coal charged, 0.1 lbs/ton coal charged, and 0.28 lbs/ton coal charged, respectively. Factors for emissions from charging, oven leakage, and coke pushing are from AP-42 and were derived from data supplied by Poland in a United Nations report on air pollution from coke plants.[45] Emission factor data from the United Nations report were determined by insufflating air samples into a sulfuric acid solution and then adding Nessler's solution. The emission factor presented in the table for coke quenching is an average of two values resulting from tests conducted on quenching towers at a Polish coke plant and at the Lorain Plant of U.S. Steel Corporation.[44,45] The values are 0.23 lbs/ton of coal and 0.33 lbs/ton of coal, respectively. An averaged value of 0.28 lbs/ton coal is used in the NAPAP inventory. The factors above are given a rating of D (as assigned in AP-42) because of the limited data from which they were developed. Activity rates for oven charging (4.8×10^7 tons coal), door leaks (2.4×10^7 tons coal), coke pushing (2.9×10^7 tons coal), and quenching (3.4×10^7 tons coal) were taken from the 1980 NEDS database[6] and were used to calculate total emissions of 7,400 tons ammonia.

AMMONIUM PHOSPHATE MANUFACTURE

Ammonium phosphates are produced by reacting phosphoric acid with anhydrous ammonia. Both solid and liquid ammonium phosphate fertilizers are produced in the United States. Ammonia emissions from production of ammonium phosphate fertilizer by ammoniation-granulation result from five process operations: reactor, ammoniator-granulator, dryer, cooler, and production sizing/material transfer. Exhaust gases containing ammonia emissions from the reactor and ammoniator-granulator are passed through primary and secondary scrubbers. Exhaust gases from the dryer and the cooler are combined and passed through cyclones and primary and secondary scrubbers. Low levels of ammonia from product sizing and material transfer operations are controlled the same way.[46]

The emission factor for ammonia from ammonium phosphate production, based on source test data from controlled phosphate fertilizer plants in Florida, is reported in AP-42 as 0.14 lbs NH_3/ton P_2O_5 produced.[46] This factor was assigned a rating of A in AP-42. The activity rate of 1.1×10^7 tons P_2O_5 produced is from the 1980 NEDS database[6] and was used to calculate emissions of 770 tons ammonia.

SUMMARY

Ammonia emission factors, activity rates, emission estimates for base year 1980, and emission factor ratings for source categories discussed above are summarized in Table 3-6. Also included in the table are Source Classification Codes (SCCs) for ammonia point and area aources. SCCs were developed by EPA for use in identifying sources in NEDS. Based on activity rates from the 1980 NEDS database, approximately 8.4×10^5 tons of ammonia are estimated to have been emitted in the U.S. in 1980.

TABLE 3-6. SUMMARY OF AMMONIA EMISSION FACTORS AND 1980 EMISSION ESTIMATES

Source	Emission factor (lbs emitted/unit)	Activity rate[a]	Units	Emissions (tons/yr)	Point source SCC[b]	Area source SCC[b]	Emission factor rating
Livestock Wastes							
Beef cattle feedlots	13	2.3×10^7	animals	150,000	3-02-020-02	77	E
Cropland spreading							
beef cattle	1.8	1.1×10^8	animals	97,000	NA	71	E
dairy cows	26	1.0×10^6	animals	130,000	NA	72	E
swine	3.1	6.3×10^7	animals	98,000	NA	73	E
sheep	2.0	NA	animals	NA	NA	NA	E
laying hens	0.19	2.2×10^8	animals	21,000	NA	75	E
broilers	0.024	3.7×10^8	animals	45,000	NA	74	E
turkeys	0.16	NA	animals	NA	NA	NA	E
Combustion Sources							
Coal	0.00056	6.3×10^8	tons coal	180	c	13,96	E
Fuel oil	0.8	NA	10^3 gallons fuel	d	e	NA	E
Natural gas							
utility boilers	3.2	NA	10^6 ft^3 gas	d	1-01-006-xx	NA	C
industrial boilers	3.2	NA	10^6 ft^3 gas	d	1-02-006-xx	NA	C
commercial boilers	0.49	NA	10^6 ft^3 gas	d	1-03-006-xx	NA	C
Mobile Sources							
leaded gasoline	0.42	NA	10^3 gallons fuel	f	NA	27-39	D
unleaded gasoline	0.63	NA	10^3 gallons fuel	f	NA	27-39	D
diesel	0.95	NA	10^3 gallons fuel	f	NA	40-44	E
Ammonium Nitrate Manufacture							
Neutralizer							
granulator	*18[h]	1.0×10^6	tons produced	9,100	3-01-027-04	NA	DE
high density prilling	*18[h]	2.3×10^6	tons produced	20,000	3-01-027-11	NA	DE
low density prilling	*18[h]	7.6×10^5	tons produced	6,800	3-01-027-21	NA	DE
Solids formation							
evaporation/concentration							
high density	*17[h]	1.2×10^6	tons produced	10,000	3-01-027-17	NA	DE
low density	*17[h]	2.2×10^5	tons produced	1,900	3-01-027-27	NA	DE
high density prill towers	*57.2	4.5×10^6	tons produced	130,000	3-01-027-12	NA	A
low density prill towers	* 0.26	5.2×10^5	tons produced	67	3-01-027-22	NA	A
granulators	*50[h]	1.9×10^6	tons produced	47,000	3-01-027-05	NA	DE
high density prill coolers	* 0.04	4.4×10^5	tons produced	9	3-01-027-13	NA	A
low density prill coolers	* 0.30	NA	tons produced	NA	3-01-027-23	NA	A
low density prill dryers	* 1.6[h]	NA	tons produced	NA	3-01-027-23	NA	DE
granulator coolers	* 1[h]	1.2×10^6	tons produced	620	3-10-027-06	NA	DE

(continued)

TABLE 3-6. (continued)

Source	Emission factor (lbs emitted/unit)	Activity rate[a]	Units	Emissions (tons/yr)	Point source SCC[b]	Area source SCC[b]	Emission factor rating
Anhydrous Ammonia Fertilizer Application	19	5.3×10^6	tons fertilizer applied	50,000	NA	76	C
Petroleum Refineries							
FCC units	* 54	3.1×10^5	10^3 barrels fresh feed	8,400	3-06-002-01	NA	B
TCC units	* 6	2.9×10^4	10^3 barrels fresh feed	87	3-06-003-01	NA	B
Reciprocating engine compressors	* 0.2	NA	10^3 ft^3 gas burned	NA	NA	NA	B
Ammonia Synthesis							
Carbon dioxide regeneration	* 2.0	1.5×10^6	tons produced	1,500	3-01-003-08	NA	A
Condensate stripping	* 2.2	1.4×10^6	tons produced	1,600	3-01-003-09	NA	A
Urea Manufacture							
Solution formation/ concentration	* 18.2	i	tons produced	NA	3-01-040-02	NA	A
Solids formation							
nonfluidized bed prilling agricultural grade	* 0.87	i	tons produced	NA	3-01-040-03	NA	A
fluidized bed prilling							
agricultural bed	* 2.9	i	tons produced	NA	3-01-040-03	NA	A
feed grade	* 4.1	i	tons produced	NA	3-01-040-03	NA	A
drum granulation	* 2.2	i	tons produced	NA	3-01-040-04	NA	A
rotary drum cooler	* 0.0051	i	tons produced	NA	NA	NA	A
Coke Manufacture							
Oven charging	* 0.02	4.8×10^7	tons coal charged	480	3-03-003-02	NA	D
Door leaks	* 0.06	2.4×10^7	tons coal charged	710	3-03-003-08	NA	D
Coke pushing	* 0.1	2.9×10^7	tons coal charged	1,400	3-03-003-03	NA	D
Quenching (contaminated water)	0.28	3.4×10^7	tons coal charged	4,700	3-03-003-04	NA	D
Ammonium Phosphate Manufacture	* 0.14	1.1×10^7	tons P_2O_5 produced	770	3-01-030-02	NA	A
Minor Point Source	NA	NA	NA	3,800	NA	NA	99
TOTAL				840,000			

(continued)

TABLE 3-6. (continued)

[a]Activity rates are from the 1980 NEDS database (Reference 6).

[b]Refers to SCCs that were in effect in conjunction with 1980 NEDS database. Many of these SCCs have since been replaced with new codes and definitions.

[c]Includes SCCs 1-01-001-xx through 1-01-003-xx, 1-02-001-xx through 1-02-003-xx, 1-03-001-xx through 1-03-003-xx, 1-05-001-02, and 1-05-002-02.

[d]NEDS activity levels for fossil fuel combusion were not applied to the related emission factors in the Emission Inventory System. Therefore, emission estimates for these sources were not included
in the 1980 NAPAP Emissions Inventory.

[e]Includes SCCs 1-01-004-xx through 1-01-005-xx, 1-02-004-xx through 1-02-005-xx, 1-03-004-xx through 1-03-005-xx, 1-05-001-05, and 1-05-002-05.

[f]NEDS activity levels for mobile sources were not applied to the related emission factors in the Emission Inventory System. Therefore, emission estimates for mobile sources were not included in the 1980 NAPAP Emissions Inventory.

[g]Rating is lower than that reported in AP-42 because of the listing of a single factor rather than a range (as in AP-42).

[h]Emission factor is from mid-point of range reported in AP-42.

[i]No activity level was reported for this SCCs in the 1980 NEDS database. Therefore, no emission estimate was calculated for this source.

[j]This SCC is for the ammoniator/granulator operation in ammonium phosphate production and may be used as the basis for the overall emission factor, as all production is based on this operation.

* - Emission factor and associated factor rating is from AP-42.

NA - Not available.

SECTION 4

COMPARISON OF NAPAP AMMONIA EMISSION FACTORS TO FACTORS DEVELOPED FOR OTHER INVENTORIES

Prior to the development of this emissions inventory document for NAPAP, similar studies were sponsored by other agencies to develop ammonia emission factors for use in other emissions inventories. These studies were sponsored by NASA Langley Research Center[20], the Electric Power Research Institute[47] (EPRI), and the Canadian Environmental Protection Service[48] (EPS), and varied widely in scope and detail. Each study attempted to gather the best ammonia emission factor data available at the time of the study for estimating nationwide emissions from anthropogenic sources (emission estimates developed by EPS were for Canada). The results of these studies are compared in this section.

Factors used in each of these studies reflect the limited database that exists concerning the release of ammonia to the atmosphere from man-made sources. Therefore, the purpose of this comparison is not to present the emission factors developed in this document as a definitive representation of the emissions that are expected from any particular facility or source. Rather, the purpose is to present the rationale that was used to select these emission factors as the best currently available, especially over other widely divergent factors.

Table 4-1 presents a summary of the ammonia emission factors developed during each of the studies. For comparison purposes, all factors for a source category are presented on the same basis (e.g. in the same units) whenever possible. In some cases, this required that emission factors developed by other inventories be converted to units consistent with the NAPAP factors. Factors developed during the NASA-, EPRI-, and EPS-sponsored studies that vary by more than an order of magnitude from the NAPAP factors presented in section 3 of this document are underlined in the table. As can be seen in the table, the largest variations in factors occur in the fossil fuel combustion, livestock waste management, and ammonium nitrate manufacturing source categories. Emission factors that vary by more than an order of magnitude are discussed in this section.

TABLE 4-1. COMPARISON OF AMMONIA EMISSION FACTORS

Source	Emission factors NASA[a]	EPRI[b]	EPS[c]	NAPAP	Units
Livestock Waste Management[d]					
Beef cattle	34	103	18	15	lbs/animal
Dairy cows	71	88	18	26	lbs/animal
Swine	7	14	1.4	3.1	lbs/animal
Sheep	--	9	1.8	2.0	lbs/animal
Laying hens	0.4	0.8	--	0.19	lbs/animal
Broilers	0.4	0.8	--	0.024	lbs/animal
Turkeys	--	2.2	--	0.16	lbs/animal
Combustion Sources					
Coal	2	1.9	2	0.00056	lbs/ton coal
Fuel oil	1	0.97	1	0.8	lbs/10^3 gallons
Natural gas	0.3	--	--	--	lbs/10^6 ft^3
utility boilers	--	3.24	--	3.24	lbs/10^6 ft^3
industrial boilers	--	3.20	--	3.20	lbs/10^6 ft^3
commercial boilers	--	0.49	--	0.49	lbs/10^6 ft^3
Mobile sources					
leaded gasoline	2.0	0.64	2.0	0.42	lbs/10^3 gallons
unleaded gasoline	--	0.64	2.0	0.63	lbs/10^3 gallons
diesel	2.0	0.95	2.0	0.95	lbs/10^3 gallons
Ammonium Nitrate Manufacture					
With granulator	--	3.8	--	--	lbs/ton
With prill tower	--	2.0	--	--	lbs/ton
Neutralizer	--	--	1.0	18	lbs/ton
Solids formation					
evaporation/concentration	--	--	1.0	17	lbs/ton
high density prill towers	--	--	0.4	57.2	lbs/ton
low density prill towers	--	--	0.4	0.26	lbs/ton
granulators	--	--	--	50	lbs/ton
high density prill coolers	--	--	--	0.04	lbs/ton
low density prill coolers	--	--	--	0.30	lbs/ton
low density prill dryers	--	--	--	1.6	lbs/ton
granulator coolers	--	--	--	1	lbs/ton
Ammonia Synthesis	--	3.2	--	--	lbs/ton
Carbon dioxide regeneration	--	--	2.0	2.0	lbs/ton
Condensate stripping	--	--	--	2.2	lbs/ton
Loading and storage	--	--	40	--	lbs/ton

(continued)

TABLE 4-1. (continued)

Source	Emission factors NASA[a]	EPRI[b]	EPS[c]	NAPAP	Units
Urea Manufacture					
Solution formation/ concentration	--	4.35	--	--	lbs/ton
Solid formation	--	--	--	18.24	lbs/ton
nonfluidized bed prilling agricultural grade	--	--	--	0.87	lbs/ton
fluidized bed prilling agricultural grade	--	--	--	2.91	lbs/ton
feed grade	--	--	--	4.14	lbs/ton
drum granulation	--	--	--	2.15	lbs/ton
rotary drum cooler	--	--	--	0.0051	lbs/ton
Ammonium Phosphate Manufacture	--	--	0.08	0.14	lbs/ton
Anhydrous Ammonia Fertilizer Application	20	--	60	19	lbs/ton
Petroleum Refineries					
FCC units	--	--	54	54	lbs/10^3 barrels
TCC units	--	--	6	6	lbs/10^3 barrels
Reciprocating engine compressors	--	--	--	0.2	lbs/10^3 ft^3 gas
Coke Manufacture					
Oven charging	--	--	0.02	0.02	lbs/ton
Door leaks	--	--	0.06	0.06	lbs/ton
Coke pushing	--	--	0.1	0.1	lbs/ton
Quenching (contaminated water)	--	--	--	0.28	lbs/ton

[a]Reference 20.

[b]Reference 47.

[c]Reference 48.

[d]NASA and EPRI emission factors are for all limestock wastes. EPS emission factors are for wastes from feedlots. NAPAP emission factors are for cattle feedlots and cropland spreading of wastes.

-- No emission factors reported. Industrial sources were accounted for in the NASA inventory although no emission factors were presented.

A study of the emission inventories based strictly on a comparison of emission factors is difficult for two reasons. First, emission factors were not pesented for certain source types in some of the inventories. For example, the EPS inventory did not include factors for ammonia from natural gas combustion while the EPRI inventory did not include a factor for ammonium phosphate manufacture. Second, emission factors were divided among a different set of source types for some source categories. An example of this is the livestock waste source category. The NASA and EPRI inventories included emission factors for all wastes resulting from most major livestock groups. Ammonia emission factors in the EPS inventory accounted for wastes from cattle, swine, and sheep feedlots only. The NAPAP inventory includes emission factors for manure from beef cattle feedlots and cropland spreading of manure from major livestock groups. Variations among the inventories in source category coverage that result in a significant difference in inventory emission estimates are discussed below.

Ammonia emission factors developed for livestock wastes are much larger in the EPRI and NASA inventories than in the EPS and NAPAP studies. Several reasons account for these differences. Some differences in the types of livestock populations and wastes covered under each inventory were discussed above. The EPRI study uses data from Adrian (1974), Leubs (1973), and Giddens (1975) and assumes that 50 percent of the N that is excreted in manure is volatilized as ammonia. This assumption does not consider other loss mechanisms such as nitrification, denitrification, and assimilation by plants. Ammonia emission factors used in the EPRI and NASA inventories do not account for a number of variables in ammonia loss rates such as manure collection systems for cropland (surface application and injection), and significant variations in the manure production of laying hens and broilers. The EPS inventory did not include emissions from wastes of chickens and turkeys. Ammonia emission factors in the EPS and NAPAP inventories for wastes from cattle, hogs, and sheep agree favorably.

The NAPAP emission factors for livestock waste management reported in this document are from Crane (1981), Hoff (1981), Westerman (1985), and Van Dyne (1978) and are based on data for manure collected and applied to cropland

as well as measured data for volatilization of ammonia from manure. These emission factors are also weighted for injection and surface application of manure. Separate emission factors for laying hens and broilers are included in the NAPAP inventory with a wide variation between the two because of the much lower average life span and smaller size of the broiler.

Within the fossil fuel combustion source category, emission factors vary for combustion of coal, natural gas, and gasoline and diesel fuel in mobile sources. The emission factor of 2.0 lbs NH_3/ton coal reported by NASA and EPS was traced through several references to a study by Wholers and Bell, SRI (1956). This latter study presents no information on the data used as the basis of the number, and consequently no further evaluation could be made. The EPRI study developed an average emission factor based on the factor of 2.0 lbs/ton from Wholers and Bell and factors of 2.6 and 1.06 lbs NH_3/ton coal, referenced from Soderlund (1977) and Muzio and Arand (1976), respectively. The factor from Soderlund was in turn referenced from Hill (1945) which obtained the data from even earlier references. On investigation, it was found that data from Muzio and Arand is the result of a short series of tests performed on a laboratory scale firetube boiler firing bituminous coal. The purpose of the tests was to examine the effect of ammonia injection on the release of nitrogen oxides (NO_x) during coal combustion. The factor of 1.06 lbs NH_3/ton of coal is based on a single sample run without ammonia injection. However, measurements from another sample run with ammonia injection resulted in a release of only 0.03 lbs NH_3/ton. The representativeness of coal combustion facilities tested and the wide variation of the results were not discussed further.

By contrast, the factor of 0.00056 lbs NH_3/ton coal reported in this document is based on tests by Bauer and Andren (1985) at two 527-megawatt coal-fired furnaces at an operating Wisconsin power plant over a six month period as discussed in section 3. Given this, and considering the age and uncertainty of the data on which ammonia emission factors used by other inventories are based, 0.00056 lbs NH_3/ton coal is considered to be an appropriate choice for use in the NAPAP inventory. The discrepancy in

reported values, however, would justify further testing with a variety of fuels to confirm or refine the emission factor for coal combustion.

The emission factor reported in the NASA study for natural gas combustion was referenced from a study on ammonia by the National Academy of Sciences (1979). This was traced back further through a series of references to factors reported over 3 decades ago with little or no description of the data from which the factors were developed. The NAPAP emission factors presented in this document for natural gas combustion were developed from tests conducted on a 200,000 Btu/hr laboratory gas combustor with data weighted for excess oxygen conditions found among utility, industrial, and commercial boilers. EPRI used the same factors as NAPAP; no factors were developed by the Canadian agency. Consequently, these emission factors were deemed the best currently available for this category.

Ammonia emissions from automobile exhausts have been reported in a number of references dating back to the early 1950's. An emission factor of 2 lbs $NH_3/10^3$ gallons fuel for gasoline and diesel-powered vehicles used in the NASA study was taken from a study by the National Academy of Sciences (1979) which referenced data traced back to over 2 to 3 decades ago. The validity of these factors is questionable based on changes in engine design and performance. An emission factor of 2.0 lbs $NH_3/10^3$ gallons fuel is also reported in the EPS study. However, this is only for vehicles equipped with three-way catalytic converters. This category is represented in studies conducted by Henein (1975), Gentel (1973), Harkins and Nicksic (1967), and Cadle and Mulawa (1980) which were used to develop the NAPAP emission factors of 0.42, 0.63, and 0.95 lbs $NH_3/10^3$ gallons fuel for leaded gasoline, unleaded gasoline, and diesel vehicles as reported in section 3 of this report. These factors are considered the best currently available for mobile combustion sources.

Table 4-1 shows a substantial difference between the ammonia emission factors for the ammonium nitrate manufacturing industry used in the EPS and EPRI studies and those described in this document. Emission factors for ammonium nitrate manufacturing were not presented in documentation supporting the NAPAP study although estimates of ammonia emissions from industrial sources were included in the NASA inventory. Emission factors listed from the EPS study were developed from questionnaires sent to Canadian manufacturing

facilities. These emissions factors do not differentiate between emissions from high density and low density prill towers and no emission factors were available for many of the other sources within the industry. The emission factors used in the EPRI study are based on data from Supplement 13 of AP-42 (1982). The NAPAP emission factors described in this document are from updated data presented in Supplement 15 of AP-42 (1984). Therefore, these factors were considered to be the best currently available.

The ammonia synthesis category reflects several differences in ammonia emission factors. As for ammonium nitrate manufacture, NASA did not present emission factors for ammonia synthesis although estimates of ammonia emissions from industrial sources were included in the inventory. The EPRI inventory presented a factor from AP-42 (1982) which has since been revised. The EPS inventory did not include a factor for condensate stripping but was the only inventory that included a factor for emissions resulting from loading and storage of ammonia. The reference for the loading/storage emission factor could not be located and therefore, this factor was not included in the NAPAP inventory. Emission factors for carbon dioxide regeneration and condensate stripping are used in the NAPAP inventory and are from recently revised data presented in AP-42 (1984).

The remaining source categories presented in Table 4-1 are ammonium phosphate manufacture, anhydrous ammonia fertilizer application, petroleum refineries, and coke manufacture. The EPRI inventory did not include factors for these sources. Emission factors for anhydrous ammonia fertilizer application included in the NASA and NAPAP inventories were similar. Again, emission factors for industrial sources were not presented in documentation supporting the NASA study although industrial emissions were included in the NASA inventory. Factors included in the EPS and NAPAP inventories for each of these sources agreed favorably.

SECTION 5
RECOMMENDATIONS

As a result of this study, some problems in the existing ammonia database have been identified. One problem is the lack of a standard test method for ammonia emissions. EPA has not sanctioned a specific test methodology and there appears to be no concensus on the best method for sampling and analysis of ammonia, especially from area sources such as livestock manure spreading.

Another area where improvement is needed is the existing emissions data for livestock waste management, ammonium nitrate production, fertilizer application, fossil fuel combustion, and coke manufacture. Data that accurately define emission rates for the variety of likely operating conditions for each of these sources are lacking. Much of the data that are available for these sources are from an inadequate small number of source tests or from research projects carried out under non-representative conditions. Often, a number of assumptions were required in order to develop emission factors from these data.

Source categories which were not included in this study but should be added to complete the database for the 1985 NAPAP Emission Inventory include human breath and perspiration, wastewater treatment, range and wild animal excrement, cigarette smoking, forest fires and natural source emissions such as swamps. Data for several of these sources may be lacking.

Following is a summary of the recommendations that resulted from this study:

- A standard test method should be developed for the sampling and analysis of ammonia emissions.
- Source test data should be gathered by reliable test methods for likely operating conditions from the following sources:
  - livestock waste management
  - ammonium nitrate production
  - fertilizer application
  - fossil fuel combustion
  - coke manufacture

- Data for the following sources should be included in the 1985 NAPAP Emission Inventory:

  - human breath and perspiration
  - wastewater treatment
  - range and wild animal excrement
  - cigarette smoking
  - forest fires
  - natural sources

REFERENCES

1. Loehr, R.C. Pollution Implications of Animal Wastes -- A Forward Oriented View. NTIS PB204218, Robert S. Kerr Water Research Center, Ada, Oklahoma, July 1968. 148 pp.

2. Peters, J.A. and T.R. Blackwood. Source Assessment: Beef Cattle Feedlots. EPA-600/2-77-107 (NTIS PB270282), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, June 1977.

3. Beef Cattle Feedlots. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1979. pp. 6.15-1 to 6.15-3.

4. Hutchinson, G.L., A.R. Mosier and C.E. Andre. Ammonia and Amine Emissions from a Large Cattle Feedlot. Environmental Quality, 11(2):288-293, 1982.

5. Fawcett, J.K. and J.E. Scott. A Rapid and Precise Method for the Determination of Urea. J. Clinical Pathology, 13:156-159, 1960.

6. National Emissions Data System. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1980.

7. Peters, R.E. and D.L. Reddell. Ammonia Volatilization and Nitrogen Transformations in Soils Used for Beef Manure Disposal. Transactions of the ASAE, 19(5):945-952, 1976.

8. Crane, S.R., P.W. Westerman and M.R. Overcash. Short-term Chemical Transformations Following Land Application of Poultry Manure. Transaction of the ASAE, 24:382-390, 1981.

9. Steenhuis, T.S., G.D. Bubenzer and J.C. Converse. Ammonia Volatilization of Winter Spread Manure. ASAE paper No. 76-4514, 1976. 17 pp.

10. Westerman, P.W., L.M. Safley, Jr., J.C. Barker, and G.M. Chescheir, III. Available Nutrients in Livestock Waste. Journal of the North Carolina Research Service, Raleigh, North Carolina, Paper No. 9998, 1985. 15 pp.

11. Hoff, J.D., D.W. Nelson and A.L. Sutton. Ammonia Volatilization From Liquid Swine Manure Applied to Cropland. Journal of Environmental Quality, 10:90-94, 1981.

12. Van Dyne, D.L. and C.B. Gilbertson. Estimating U.S. Livestock and Poultry Manure and Nutrient Production. ESCS-12, U.S. Department of Agriculture, Washington, D.C., 1978. 145 pp.

13. Statistical Abstracts of the United States, 97th Edition, U.S. Department of Commerce, 1976. pp. 670-673.

14. Bituminous and Subbituminous Coal Combustion. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1982. p. 1.1-6.

15. Hill, W.H. Chemistry of Coal Utilization. Wiley and Sons, New York, New York, 1945. p. 1008.

16. Wohlers, H.C. and G.B. Bell. Literature Review of Metropolitan Air Pollutant Concentrations - Preparation, Sampling and Assay of Synthetic Atmospheres. Stanford Research Institute, Menlo Park, California, 1956. p. B-8.

17. The Acidic Deposition Phenomenon and Its Effects - Critical Assessment Review Papers, Volume I - Atmospheric Sciences. EPA-600/8-83-016F, U.S. Environmental Protection Agency, Washington, D.C., July 1984. p. 2-39.

18. Ammonia. National Research Council, National Academy of Sciences, Washington, D.C., 1979.

19. Cass, G.R., et al. The Origin of Ammonia Emissions to the Atmosphere in an Urban Area. Environmental Quality Laboratory, California Institute of Technology, Pasadena, California, 1982.

20. Harriss, R.C. and J.T. Michaels (NASA). Sources of Atmospheric Ammonia. Proceedings Second Symposium, Composition of the Nonurban Troposphere, American Meteorological Society, Williamsburg, Virginia, May 1982. pp. 33-35.

21. Robinson, E. and R.C. Robbins. Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants. American Petroleum Institute, New York, New York, February 1968.

22. Hovey, H.H., A. Risman, and J.F. Cunnan. The Development of Air Contaminant Emission Tables for Nonprocess Emissions. Journal of the Air Pollution Control Association, 16(7):362-366, July 1966.

23. Muzio, L.J. and J.K. Arand. Homogeneous Gas Phase Decomposition of Oxides of Nitrogen. Electric Power Research Institute, 1976. pp. 60-61, C-12.

24. Bauer, C.F. and A.W. Andren. Emissions of Vapor-Phase Fluorine and Ammonia from the Colombia Coal-Fired Power Plant. Environmental Science and Technology, 19(11):1099-1103, 1985.

25. Fuel Oil Combustion. In: Compilation of Air Pollution Emission Factors, AP-42. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1982. pp. 1.3-1 to 1.3-5.

26. Magill, P.L. and R.W. Benoliel. Air Pollution in Los Angeles County. Industrial and Engineering Chemistry, 44:1347-1351, 1952.

27. Reference 23, pp. 5, C-22, and C-23.

28. Natural Gas Combustion. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, August 1982. pp. 1.4-1 to 1.4-4.

29. Miner, S. Air Pollution Aspects of Ammonia. APTD 69-25. National Air Pollution Control Administration, Washington, D.C., 1969.

30. New York State Air Pollution Inventory Program Plan. N.Y. State Dept. of Health, Bureau of Air Pollution Control Services, 1958.

31. Reference 23, Appendix C.

32. Henein, Naeim A. The Diesel as an Alternative Automobile Engine. Wayne State University, SAE Paper 750931, 1975. pp. 4-6.

33. Gentel, J.E., O.J. Manary, and J.C. Valanta. Characterization of Particulates and Other Non-Regulated Emissions from Mobile Sources and the Effects of Exhaust Emissions Control Devices on these Emissions. EPA/APTD-1567 (NTIS PB224243), U.S. Environmental Protection Agency, Ann Arbor, Michigan, 1973. pp. 81-85, 106.

34. Harkins, J.H. and S.W. Nicksic. Ammonia in Auto Exhaust. Environmental Science and Technology, 1(9):751-2, 1967.

35. Cadle, S.H. and P.A. Mulawa. Low Molecular Weight Aliphatic Amines in Exhaust from Catalyst-Equipped Cars. Environmental Science and Technology, 14(6):721, 1980.

36. Energy and Environmental Analysis, Incorporated. The Motor Fuel Consumption Model: Eleventh Periodical Report. Contract No. 68-03-1865, Work Assignment No. 8, U.S. Environmental Protection Agency, Motor Vehicle Emission Lab, Ann Arbor, Michigan, 1984. p. B-2.

37. Ammonium Nitrate. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1984. pp. 6.8-1 to 6.8-8.

38. Denmead, O.T., J.R. Simpson, and J.R. Freney. A Direct Field Measurement of Ammonia Emission After Injection of Anhydrous Ammonia. Soil-Sciences Society of America Journal, 41:1001-1004, 1977.

39. Emissions to the Atmosphere from Petroleum Refineries in Los Angeles County. Publication No. LAV-APCD/EMI-A-P, Air Pollution Control District, County of Los Angeles, 1958.

40. Masser, C.C. Petroleum Refining. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, December 1977. pp. 9.1-1 to 9.1-9.

41. Synthetic Ammonia. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, July 1979. p. 5.2-1.

42. Urea. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1984. pp. 6.14-2 to 6.14-5.

43. Coke Manufacturing. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1980. p. 7.2-1.

44. Griffin, H.F., et al. Characterization Program for Coke Quench Tower Emissions. In: Proceedings-Control of Air Emissions from Coke Plants, Air Pollution Control Association, April 1979. pp. 128 and 136.

45. Air Pollution by Coking Plants. United Nations, New York, New York, 1968. pp. 14-19.

46. Ammonium Phosphates. In: Compilation of Air Pollution Emission Factors, AP-42. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, October 1980. p. 6.10.3-1.

47. Steven Heisler, ERT, Newbury Park, California. Personal communication with Graham Fitzsimons, GCA/Technology Division Inc., Chapel Hill, North Carolina, June 12, 1986.

48. National Inventory of Natural and Anthropogenic Sources and Emissions of Ammonia (1980), Environmental Protection Service, Environment Canada, February 1985.

APPENDIX A

CRITERIA FOR ASSESSING EMISSION FACTORS

This appendix describes the criteria that were used to assess the quality of the ammonia emission factors presented in Section 3. The purpose of the ratings is to provide a qualitative indication of the reliability of the emission factors. Criteria used to assess the emission factors are listed below.

DISCUSSION OF CRITERIA

- Test methods used: Most emission factors are determined from either source tests, industry surveys, mass balances, or engineering estimates. The accuracy of these methods is dependent on several different parameters which change from one emission source to another.
  - Source Test: In source testing, samples are taken directly from the source emitting the pollutant. Accurate approved test methods should have been used whenever possible. If an unapproved method or an outdated method was used the quality of the emission factor should be questioned.
  - Industry Survey: In a survey EPA submits a series of questions to a plant or site that is emitting the pollutant in question. They voluntarily fill out and return the questionnaire to the surveyor. To obtain accurate information the questions must be worded carefully so that the correct and desired information will be given. If consistent results are reported by the participants, the information may be considered accurate. To effectively assess the quality of an emission factor, the survey methodology should be known.
  - Engineering Estimate: An engineering estimate is based on process information available to the engineer. The engineer makes several assumptions based on his experience and knowledge of the process. Using these assumptions and other available information he estimates an emission factor. This method of determining an emission factor is generally the most inaccurate. However, with adequate background information, frequently an accurate estimate can be made.
- Size of Data Base: The emission factor becomes increasingly accurate as the data base from which the factor was determined expands. Emission factors constructed on information from one source have less credibility than those from several sources.

- Data Base Represents a Good Cross Section of Industry: An average emission factor should be determined from a cross section of the industry. A good cross section is related to the size of the data base. However, a large data base does not insure a good cross section, and an excellent cross section is possible from a small data base.

- Age of Data: For the following reasons some emission factors quickly lose credibility:

  - The sampling and testing methods may have been proven invalid and as better methods are developed, inherent flaws in previously used methods are discovered.

  - Innovations in technology occur in most industries on a regular basis. Consequently, the process parameters used when the emission tests were performed may differ significantly from what is currently used in the industry. Control systems may be more efficient, fuel feed and production rates may differ, the composition of pollutants may be significantly different, etc. As a result, the old emission factor may no longer apply.

  - New laws and regulations may be passed which would significantly affect the emissions from a source.

RATING SYSTEM

A rating system, analogous to the AP-42 system, was developed to grade each emission factor. Due to the variability in the type of information contained in the reference used to assign emission factors, a good deal of subjective engineering judgment was used in giving each factor a grade.

Emission factors for each process were given a rating of A through E, a rating of A representing the more reliable emission factor and a rating of E the lesser.

A qualitative description of each rating is as follows:

- A

  - Large data base from surveys or source tests on several different studies was used.

  - Data base covers a good cross section of the industry.

- Emissions were measured using currently valid test methods.
- Emission factors were determined by mass balance based on sound measurement.

• B

- Data base is fairly large, however, it is not clear that it represents a good cross section of the industry.
- Emission factor was measured using valid test methods at the time the test was performed. However, tests have since been revised.
- Engineering estimate based on sound accurate information

• C

- Data base consists of a few good sources.
- Data may or may not be representative of the industry.
- Engineering estimates based on accurate information. However, information is not extensive or complete.

• D

- Data base is small. If one sample, it was a representative site.
- Data base may not be representative of industry.
- Unapproved test methods may have been used.
- Engineering estimates are based on information where accuracy is questionable.

• E

- Data base is small. Results conflict with each other.
- Any sources tested are not representative of the industry.
- Engineering estimates are based on very little reliable information.

The ratings above are referred to throughout section 3 in the discussion of specific emission factors.